New Approach to Modeling Mixtures Based on Helmholtz Energy Equations for the Components

Jan Hrubý[1, S, C], Aleš Blahut[1] and Václav Vinš[1]

[1]*Thermodynamics, Institute of Thermomechanics of the Czech Academy of Sciences, Prague 8, Czechia*
hruby@it.cas.cz

Multiparameter equations of state formulated in terms of the Helmholtz energy enable computation of all thermodynamic properties essentially within the uncertainty of the underlying experimental data. They are implemented in thermophysical property databases such as REFPROP, TREND, and CoolProp. The presently used model for computing residual properties of mixtures [1] is efficient in modeling complex mixtures. However, virial coefficients computed from this model do not obey the rigorous mixing rules [2]. We further analyzed this problem and provided a new general model avoiding this deficiency [3].

The new model [3] is based on Helmholtz energy equations for the components and for the so-called cross-components, which represent interactions of unlike pairs of molecules. The equations for the components and cross-components are combined in a quadratic form of concentrations or, equivalently, mole fractions. This is to some extent analogous to the current method [1]. The main difference is in avoiding the corresponding-states based scaling of temperature and density variables. Instead, we introduce general density and temperature scaling functions which can be expanded, for low densities, into a Taylor series in terms of molar concentrations of individual components. We showed that when the method is applied for a cubic equation of state with a simple choice of the scaling functions, the same result is obtained as when using the classical van der Waals mixing rules.

In this work, we use the same simple scaling functions in combination with multiparameter Helmholtz energy equations for the components. The residual Helmholtz energy for the cross-component is modeled as an arithmetic average of the functions for the two corresponding components. Scaling volume and temperature for the cross-component are chosen, respectively, as an arithmetic and geometric average of the pure fluid parameters. With this purely predictive set up (no adjustment to mixture data), density in gas, liquid, and supercritical regions can be reproduced for mixtures of simple components (such as alkanes, argon, nitrogen) with reasonable accuracy. Computations of vapor-liquid phase equilibria (VLE) revealed an important requirement on the equations of state of the components: at least the lower-boiling components must be represented with equations yielding a proper van der Waals loop with one minimum and one maximum. Unfortunately, the present Helmholtz energy formulations generally show more complex (rather arbitrary) behavior in the metastable/unstable region. We developed an ad-hoc cubic equation for butane and we used it to model VLE for butane and methane. The computations compare favorably with experimental data. The accuracy of predictive computations largely depends on the quality of the equations of state including the metastable/unstable region.

For more complex mixtures, dedicated Helmholtz energy equations for the cross-components and more sophisticated scaling relations need to be developed.

References

1. E.W. Lemmon, R. Tillner-Roth, *A Helmholtz energy equation of state for calculating the thermodynamic properties of fluid mixtures*, Fluid Phase Equilib. 165, 1 (1999). https://doi.org/10.1016/s0378-3812(99)00262-9
2. A. Jäger, C. Breitkopf, M. Richter, *The Representation of Cross Second Virial Coefficients by Multifluid Mixture Models and Other Equations of State*, Ind. Eng. Chem. Res. 60, 9286 (2021). https://doi.org/10.1021/acs.iecr.1c01186
3. J. Hrubý, *A General Model for Thermodynamic Properties of Fluid Mixtures Based on Helmholtz Energy Formulations for the Components. Virial Expansion and Reduction to van der Waals Mixing Rules,* Int. J. Thermophys. 44, 130 (2023). https://doi.org/10.1007/s10765-023-03237-8